DIP COATING PROCESS

Silicon Sheet Growth Development for
the Large-Area Silicon Sheet Task
of the Low-Cost Silicon Solar Array Project

Quarterly Report No. 1

by

J.D. Heaps, R.B. Maciolek, W.B. Harrison, and H.A. Wolner

Period Covered: 10/21/75 - 12/18/75

Published December 19, 1975

JPL Contract No. 954356

Honeywell Corporate Research Center
10701 Lyndale Avenue South
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This work was performed for the Jet Propulsion
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ABSTRACT

The objective of this research program is to investigate the technical and economic feasibility of producing solar-cell-quality sheet silicon by dip-coating one surface of carbonized ceramic substrates with a thin layer of large-grain polycrystalline silicon. The initial effort has concentrated on the design and construction of the experimental dip-coating facility required to carry out this investigation. The design has been completed and its experimental features are discussed in the report. Current status of the program is reported, including progress toward solar cell junction diffusion and miscellaneous ceramic substrate procurement.

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SUMMARY

An experimental dip-coating facility has been designed and is presently 70 percent constructed. This facility will be used to pursue a research program which will investigate the technical and economic feasibility of producing solar-cell-quality sheet silicon by dip-coating inexpensive carbonized ceramic substrates with a thin layer of polycrystalline silicon. The dip process methods to be developed will be directed toward minimum-cost processing of silicon into sheets of a quality suitable for producing solar cells with a terrestial conversion efficiency of 10 percent or greater.

Through the course of the program, the suitability of various ceramic substrates will be investigated, and substrate carbonization techniques will be developed. Dip-coating growth parameters will be optimized in an effort to produce large crystalline grains with minimal dislocation densities. The physical and electrical properties of the silicon coatings will be evaluated.

To adequately investigate dip-coating growth parameters, the following research capabilities have been designed into the facility now being constructed:

- An alternate temperature-control thermocouple which can be lowered into the silicon melt during the dip-coating procedure.
- A programmable, variable-speed dipping-pulling mechanism.
- A direct two-pen chart recording of substrate dip-pull rates and temperature.
- An "after heater," if so desired, located immediately above the silicon melt.

- A capability of orienting the substrate at an angle while performing the dip-pull operation.
- A gas lock chamber for loading uncoated substrates and removing coated ones without shutting down the melt power.
- An ultrapure graphite silicon melt heating element powered by a 25KW SCR-controlled power supply.
- A cleanable viewing port for visually observing the meniscus at the surface of the melt as the substrate is being withdrawn.

A lesser parallel effort pursued during this reporting period was that of preparing a diffusion furnace in which solar cell junctions can be produced. This furnace will initially be used to (1) reacquire state-of-the-art single-crystal solar cell efficiencies and (2) evaluate the performance of the unique p-n layer top-surface electrode made necessary by the electrically insulating substrate upon which the silicon is coated.

During this reporting period numerous ceramic materials and ceramic formulations have been ordered. They include:

- Mullite substrates
- 85% and 96% alumina substrates
- Zirconia substrates
- Cordierite substrates
- Mullite formulation
- Cast silica material
- Molded mullite fiber material
- Calcium aluminate substrates

INTRODUCTION

This research program commenced October 21, 1975. Its purpose is to investigate the technical and economic feasibility of producing solar-cell-quality sheet silicon by dip-coating inexpensive ceramic substrates with a thin layer of polycrystalline silicon. The dip-coating methods to be developed are to be directed toward a minimum-cost process with the objective of producing solar cells with a terrestial conversion efficiency of 10 percent or greater.

Previous to this program the Honeywell Corporate Research Center experimentally demonstrated that silicon coatings could be applied to carbonized ceramic substrates by immersing them into molten silicon and subsequently removing them at a pulling rate of ~1 cm/second. Honeywell, Inc., has since filed for patent rights on this process.

Layers resulting from this coating technique had growth-parameter-dependent thicknesses ranging from 25 to 100 micrometers, with crystalline grains substantially larger than the layer thickness.

This program is continuing this previous work, with efforts directed toward the following major tasks:

1. Design and construction of an experimental dip-coating facility.
2. Definition of an inexpensive ceramic substrate material whose properties are compatible with silicon and the dip-coating process.
3. Development of a substrate carbonization technique.
4. Characterization of the optimum dip-coating growth parameters to maximize grain size and minimize individual crystallite dislocation density.

5. Characterization of the physical and electrical properties of the silicon coatings.

6. Evaluation of solar cells fabricated from the silicon coatings.

To date, major emphasis has been on the design and construction of the coating facility needed to perform the major objectives of this program. As such, no theoretical or experimental results have yet been accomplished. This document will, therefore, report the program's current status and discuss the research capabilities of the dip-coating facility being constructed.

TECHNICAL DISCUSSION

EXPERIMENTAL DIP-COATING FACILITY

To systematically perform an investigation of the growth parameters which affect grain size, dislocation density and layer purity, a flexible and reliable experimental facility must be assembled. To the greatest extent possible, the facility should be designed and constructed such that its characteristics do not further complicate the problems to be solved. The facility should accurately and reporducibly perform its functions, enabling the researcher to form positive conclusions concerning the experimental results. Likewise, since modifications are expected from time to time, sufficient design flexibility should permit such modifications to be performed with minimum time and expense. With these objectives in mind, the design of the facility was completed on schedule.

The following research capabilities were included in this design:

- An alternate temperature-control thermocouple which can be lowered into the silicon melt during the dip-coating procedure. This thermocouple will be fitted with a replaceable quartz cover of semiconductor purity.

  The dip-coating work done prior to this investigation strongly suggested that melt temperature and pull rate are probably the two most important parameters which influence grain size. It is, therefore, improtant that melt temperature not only be measured, but that it also be controlled with minimum thermal lag. By immersing a thermocouple into the melt, once the silicon has been melted, the above conditions can best be satisfied.

- A programmable, variable-speed dipping and pulling mechanism.

  It likewise is known that the pulling rate for satisfactory coatings is melt-temperature dependent and thus must be variable. The previous study further suggested that a high degree of nucleation from previously grown silicon was occurring as the substrate was being withdrawn from the melt. Perhaps, then, it may be beneficial to also have the capability of programming the pulling rate such that, as the substrate emerges from the melt, the pulling rate is increased by an amount corresponding to the crystalline grain development. This feature will be accomplished by a programmable cam on the dipping and pulling mechanism.

- A direct two-pen chart recording of the substrate dip-pull rates and temperature, both with reference to the surface of the melt.

  To efficiently characterize the optimum growth parameters, it is mandatory that the growth conditions be accurately recorded for each sample substrate that is dip-coated. By doing so, as the physical properties of each coated sample are analyzed with respect to their particular growth conditions, positive direction can be given to the investigation. To accomplish this capability, the dipping and pulling mechanism is designed to provide an electrical readout which when combined with recorder's chart speed provide dip-pull rate information.

- An "after heater," if so desired, located immediately above the silicon melt.

  This research capability could increase control of the solidification process and promote continued grain growth as the substrate is pulled through this elevated temperature zone. Further, by elevating the temperature above the melt, those ceramic substrates more

susceptible to thermal shock will be preheated prior to their immersion into the molten silicon.

- A capability of orienting the substrate at an angle while performing the dip-pull operation.

  To date, there are no well-defined theories which suggest angle dipping may enhance grain size, but intuitively one expects that dipping an angle-oriented substrate would certainly modify the liquid-solid interface, perhaps in a beneficial way. Therefore, should this later be considered a desirable modification, provisions for this capability should, at this time, be designed into the facility.

- A gas-lock chamber which permits the operator to load uncoated substrates and remove coated one without shutting down the melt power.

  This feature is made possible by a large vacuum gate valve which is located between the dip-coating chamber and the gas-lock chamber. The gas-lock chamber can be readily purged with argon prior to opening the gate valve.

- An ultrapure graphite silicon melt-heating element powered by a 25KW SCR-controlled power supply.

  This melt heater is sufficiently over-powered to permit rapid melting of the silicon charge. In addition to saving time, it is generally believed that a cleaner melt surface is attainable by rapid melting procedures.

- A cleanable viewing port for visually observing the meniscus at the surface of the melt as the substrate is being withdrawn.

The construction of the dipping-pulling mechanism which performs two of the above functions has been completed. The construction of the remainder of the facility is approximately 70 percent finished.

Figure 1 is a sectional drawing of the facility. The graphite silicon melt heater assembly and its 25KW power supply was engineered and constructed by Intermat Corporation (an enterprise of the Arthur D. Little Company). It was purchased by Honeywell as a capital equipment expenditure. The melt heater is presently being assembled by Intermat on the base plate of the melt chamber. It is scheduled to be shipped to Honeywell on December 19, 1975. The power supply was delivered to Honeywell on December 18, 1975.

The major portion of the facility is constructed from stainless steel. To minimize contaminating insulation materials, the graphite heating elements are surrounded only by ultrapure graphite heat shields and ultrapure carbon felt. As such, all surfaces of the melt and dipping chambers are water cooled. Likewise the heating element electrodes and copper power leads are water cooled.

A quartz-covered thermocouple will be positioned against the back surface of the substrate to be coated. Its function will be to indicate the substrate temperature and identify its position with respect to the surface of the melt. The quartz tubing covering this thermocouple can readily be replaced following each coating operation.

DIFFUSION FURNACE

During this reporting period a quartz diffusion furnace liner was procured and tubing end caps and sample and dopant holders were fabricated in readiness for solar cell junction work planned for next quarter.

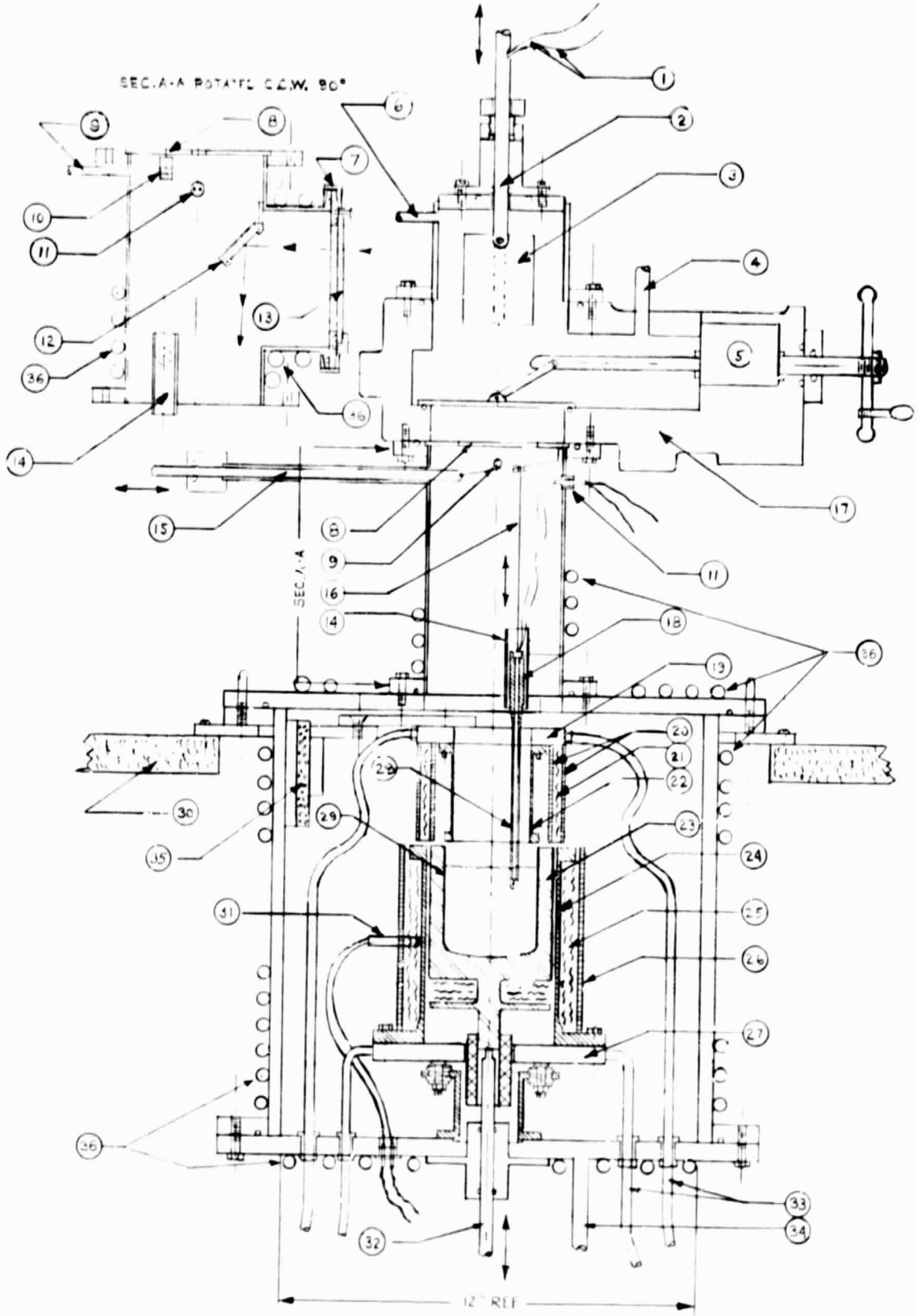

Figure 1a. Experimental Dip-Coating Facility - Sectional View
(See Figure 1b for nomenclature)

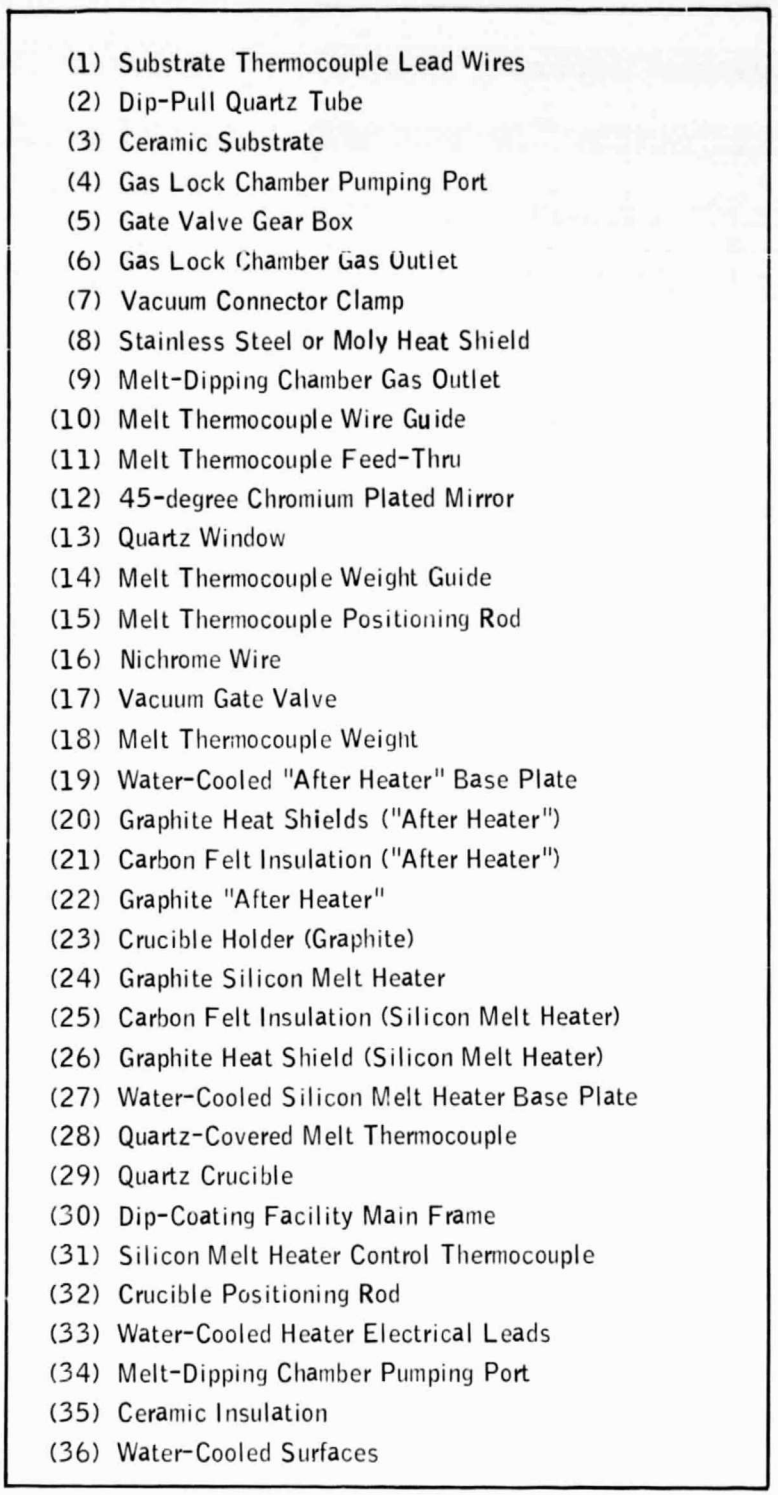

Figure 1b. Experimental Dip-Coating Facility - Nomenclature

CERAMIC SUBSTRATE PROCUREMENT

During this portion of the program a suitable, inexpensive substrate material was sought which is compatible with the silicon dip-coating process. In the coating process the substrate must withstand the chemical attack of molten silicon without dissolving and contaminating the silicon melt or the silicon coating deposited on the substrate. However, sufficient wetting to obtain mechanical or chemical adherence between the silicon and substrate must be achieved and maintained throughout the rest of the production process required for the final large-area photovoltaic energy panels. The thermal expansion of the substrate also must match that of the silicon close enough to maintain stability of the coated substrate throughout its life cycle.

One material which has shown initial success in small sections is mullite tubing; therefore, the initial effort this quarter has been to achieve this material in flat sheets. Prior to the advent of high alumina ceramics, mullite and several other ceramic insulating materials were commonly used in flat sheets; now, however, this material in flat sheets is virtually nonexistent.

The American Lava Division of Minnesota Mining and Manufacturing has graciously agreed to supply 2.5 x 2.0-inch substrates of an experimental mullite formulation which has not yet been released for production. These, along with a zircon, cordierite, 85 percent alumina and 96 percent alumina substrates have been ordered. The McDaniel Corporation was requested and has agreed to supply their mullite formulation in a wet plastic state as commonly used for their extrusion operation. This material will be used to roll sheets of material into various sizes. The use of this material, which has already shown initial success, will test the feasibility of fabricating large thin-sheet material. If this approach can be shown to be feasible, it will very likely yield a low-cost substrate. Rolling, drying and firing of this material will be done at the Ceramics Center.

Three other low-cost approaches being considered are outlined below:

- Cast Silica - Materials for the evaluation of a casting approach also have been ordered. Two grades of fused silica grain have been ordered from Glass Rock, Inc., and these will be used to formulate a material which will be cast into thin sheets. Such material would require a lower firing temperature than mullite and would potentially offer a second low-cost substrate material for this program.

- Molded Mullite Fiber - Fiberfax sheet material has been obtained and will be used with a refractory binder phase to produce a low-cost sheet material. Several binder phases will be considered.

- Calcium Aluminate Substrate - Materials for producing a calcium-aluminate-bound alumina ceramic substrate also have been obtained and are being fabricated into thin substrates. This is another material which requires only low curing temperatures to yield a ceramic which will withstand 1700°C.

Thus a wide variety of materials as shown in Table 1 have been ordered or received for this program which potentially will yield a low-cost substrate for this program.

Table 1. Properties of Typical Ceramic Substrates

Type Material	Density (gm/cc)	Thermal Exp. $X10^{-6}/°C$ 25-900°C	Temp. Limit (°C)	Flexural Strength (psi)
Mullite, MU33[a]	3.3	4.8	1500	22,000
Fiberfax[b]	0.4	4.8	1300	nil
Zircon, 475[c]	3.7	4.9	1370	22,000
Cordierite, 202[c]	2.1	2.8	1250	8,000
94% Al_2O_3, 771[c]	3.62	7.4	1500	44,000
96% Al_2O_3, 614[c]	3.70	7.9	1550	46,000
99.5% Al_2O_3, 772[c]	3.89	7.7	1600	65,000
Polygranular SiO_2[d]	1.94	0.5	1200	20,000

a McDaniel Corporation
b Carborundum
c American Lava Corporation
d Glass Rock Incorporated

CONCLUSIONS

Barring unforeseen problems, the experimental dip-coating facility should be completed on schedule, and all parts and materials required to perform the initial dip-coating operation (scheduled for January 21, 1976) should be in-house prior to this target date.

PROJECTED SECOND QUARTER ACTIVITIES

GENERAL

During the next quarter, the dip-coating facility will be completed and placed into operation. Initially the influence of two primary solidification parameters -- melt temperature and pull rate -- on the grain size and growth rate of silicon solidified on carbon-coated ceramic substrates will be studied with the object of learning how to grow the largest possible grain size at the fastest possible rate.

Increasing melt temperatures should suppress nucleation and hence promote large grain growth. However, high melt temperatures are not usually conducive to high growth rates during controlled solidification unless elaborate precuations have been taken to remove both the super heat from the melt and the heat of solidification at the liquid-solid interface. If these precautions are not taken, spontaneous nucleation occurs in the liquid film as it cools, and control of the solidification process is lost. Therefore, there exists an optimum set of conditions -- melt temperature and pull rate -- for the rapid growth of large-grained silicon.

To define such optimum conditions, the pull rate and melt temperature will be varied systematically. The films will be characterized with regard to grain size and growth morphology. Changes in structure of the films will be correlated with the imposed changes in the solidification parameters in an interactive fashion to reach optimum solidification conditions.

In addition to the above growth parameter studies, single-crystal solar cells will be fabricated for the purpose of reacquiring state-of-the-art conversion efficiencies and to evaluate the performance of the unique p-n layer top-surface electroding technique imposed by the electrically insulating substrate.

Further effort next quarter also will be concentrated on testing and evaluating the procured substrates and on an evaluation of low-cost fabrication approaches for mullite, fiberfax, silica and calcium aluminate.

THERMAL AND PHYSICAL PROPERTIES

The thermal and physical properties are not as critical as low cost, but they, too, play an important role in determining the suitability of a given substrate. For instance, thermal expansion coefficient, thermal conducivity, physical strength, and surface characteristics such as grain size, texture, and smoothness are expected to be important parameters which will determine how controllably the silicon coating can be deposited on the substrate. More insight on each of these important parameters is given below.

Stability

The highly acidic nature of silicon suggests neutral or acidic-type substrates such as mullite ($3Al_2O_3 \cdot 2SiO_2$) or alumina (Al_2O_3) commonly used for electronic substrates. Other possible materials include zircon ($ZrO_2 \cdot SiO_2$), cristobolite (SiO_2), or materials with small amounts of basic oxides such as cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$). Any of these materials are expected to have the short-time stability necessary for it to achieve a silicon coating. However, the time of contact will be critical for the low-temperature-resistant materials such as cordierite. The properties of these potential substrates were given in Table 1.

Thermal Expansion

The materials listed in Table 1 offer various thermal expansion coefficients which are approximately equal to or slightly higher than silicon. Since mullite has been used at Honeywell for producing ceramic-to-silicon

seals, we will evaluate material with slightly higher and lower expansion coefficients than mullite.

Physical Strength

All of these materials are equal to or greater in strength than glass; therefore, we expect the strength to be adequate.

Surface Characteristics

Variations in surface texture, grain size and roughness can be achieved in the ceramic substrates. Dip-coating parameters are expected to largely determine the silicon's grain size; however, grain size of the substrate may also play an important role in the size and orientation of the polycrystalline silicon film produced. If such dependence is found, then the texture of substrates may be critical in controlling the number of nucleation sites in the silicon. In this instance, large grains probably would be more appropriate than a surface with many small grain and surface defects, which each would tend to nucleate s small silicon crystallite. An alternate approach would introduce a second phase of relatively large crystallites into the substrate material.

PROGRAM STATUS UPDATE

Updated versions of the Program Plan, Program Labor Summary, and Program Cost Summary are presented in Figures 2, 3, and 4.

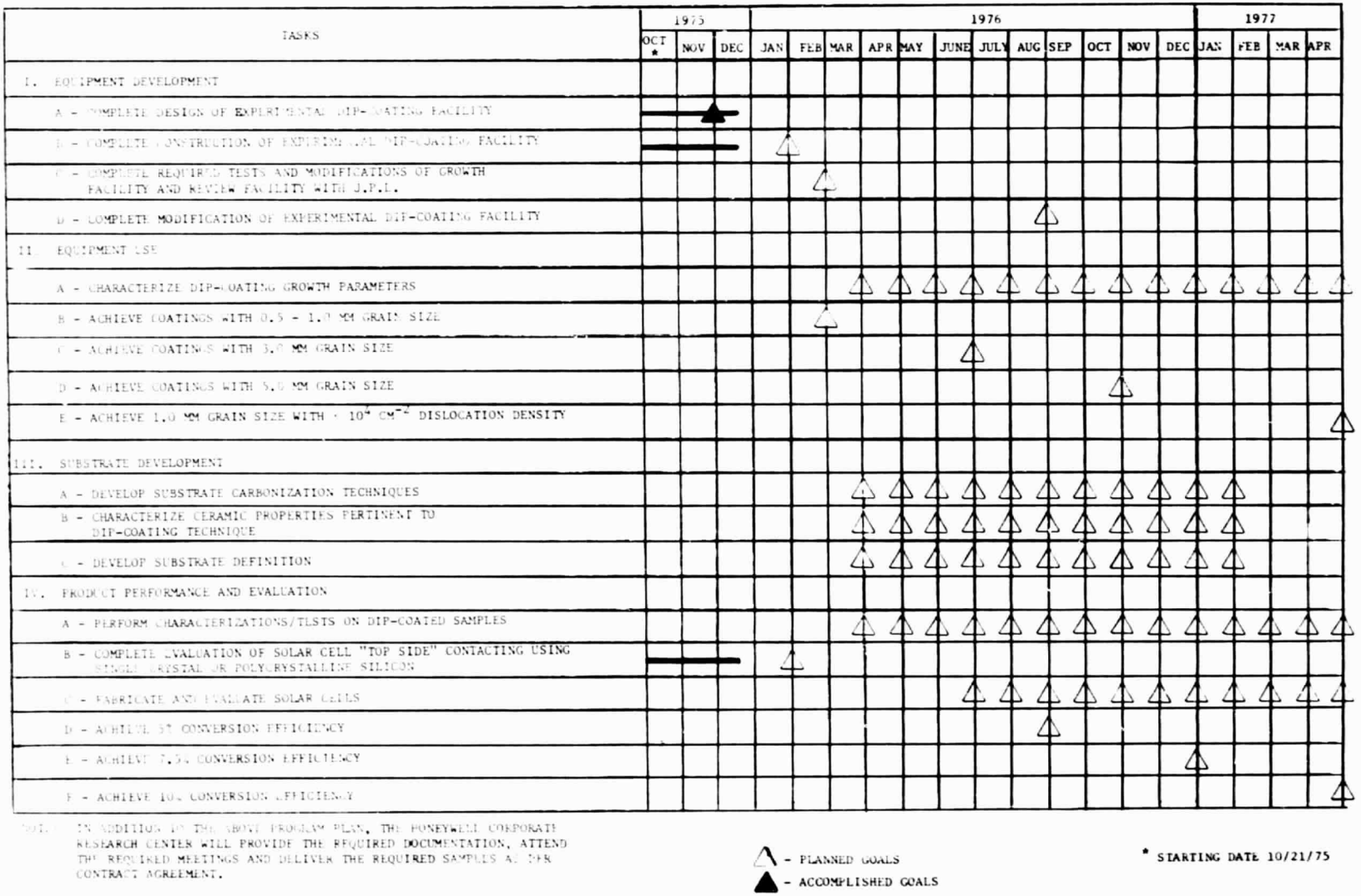

Figure 2. Updated Program Plan

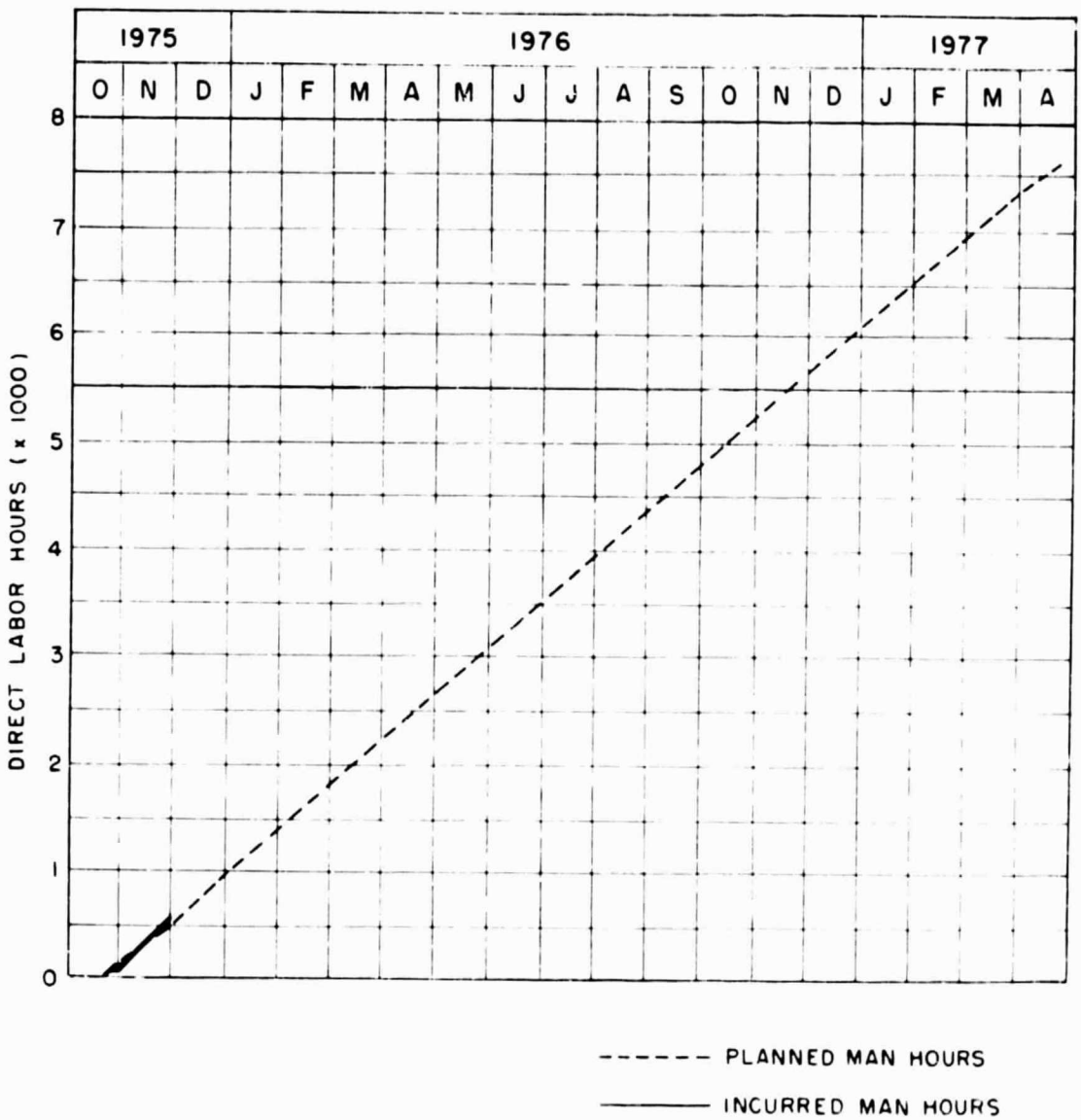

Figure 3. Updated Program Labor Summary

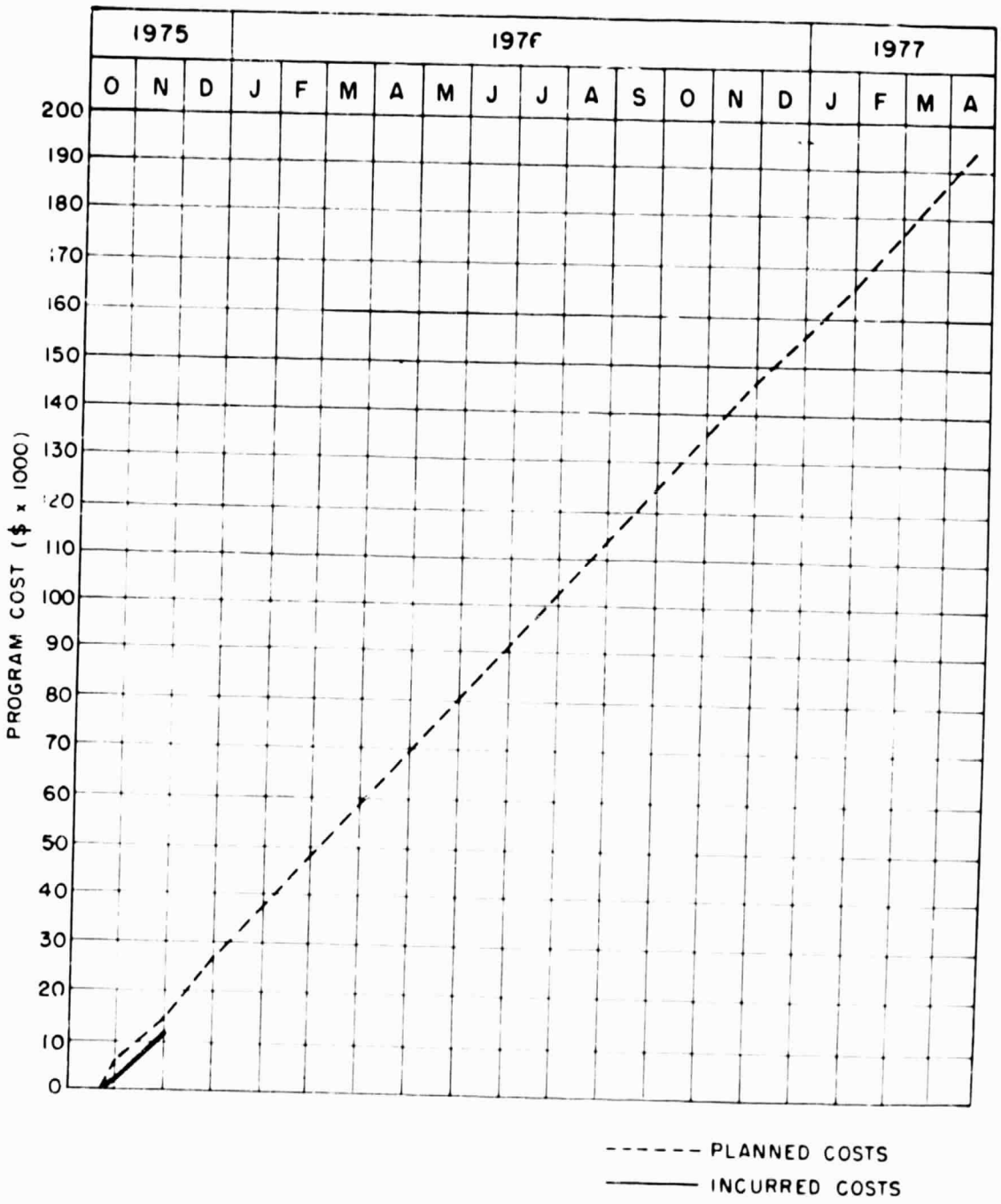

Figure 4. Updated Program Cost Summary